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(54) Title of the invention Method for
 Manufacture of
 Optical Element

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A detailed description

1. Title of the invention

Method for Manufacture of Optical Element.

2. Scope of patent claims

(1) The method for manufacture of optical element has the following characteristics. Namely, in the method to manufacture optical element by subjecting a resin composite formed from polymer

component containing aromatic vinyl unimer units, as its main constituent and polyphenylene ether component; to fusion molding, polyphenylene ether component is the stabilized polyphenylene ether.

(2) The method described above in claim number (1) in which the stabilized polyphenylene ether is the polyphenylene ether that is regulation treated by α pinene.

(3) The method described above in claim number (1) in which the stabilized polyphenylene ether is the polyphenylene ether whose terminal hydroxide radicals are capped.

3. Detailed description of the invention

(Industrial applicability)

The present invention relates to the optical element having satisfactory thermal stability. For example, the present invention relates to the optical element of optical disk baseboards that carry out recording and

regeneration of information optically and optical cards,
lenses, prisms etc.

(Techniques of the past)

The optical element formed from polymer originating in aromatic vinyl unimer and polyphenylene ether has been presented in USP 4,373,065.

An optical disk baseboard formed from mixed composite of polystyrene and polyphenylene ether has been proposed in this (patent).

However, concrete manufacture of optical element has not been described in USP 4,373,065 and only simple methods such as injection molding, cast molding have been described.

(Problems the invention solves)

Combination of polymer originating in aromatic vinyl unimer and polyphenylene ether has the characteristic of --- optical anisotropy and having low birefringence (double refraction).

Moreover, in the case of using fusion molding as the method to manufacture optical element, dependency of its birefringence (double refraction) on the molecular weight of polymers is large.

The resin composite containing polyphenylene ether has high glass transition temperature due to which at the time of molding this resin composite by fusing it, thermal deterioration takes place.

Molecular weight of a part of polyphenylene ether increases by thermal deterioration and therefore, optical anisotropy increases and birefringence (double refraction) increases.

Moreover, unevenness and strain get generated in the resin composite mentioned above, which brings about deterioration of light permeability.

Furthermore, thermal deterioration exerts bad influence on it as optical element such as occurrence of coloration or generation of oxide.

(Method to solve the problems)

The present invention relates to the method for manufacture of optical element that has the following characteristics. Namely, in the method to manufacture optical element by subjecting a resin composite formed from polymer component containing aromatic vinyl unimer units, as its main constituent and polyphenylene ether component, to fusion molding, polyphenylene ether component is the stabilized polyphenylene ether.

The resin composite of the present invention is the mixture of polymer containing aromatic vinyl unimer units as its main constituent and stabilized polyphenylene ether, or the material formed by stabilizing the polyphenylene ether component of block copolymer or graft copolymer formed from polymer containing aromatic vinyl unimer units as its main constituent and polyphenylene ether component, or its mixture.

As regards the polymer containing aromatic vinyl unimer

units used in the present invention, aromatic vinyl unimer independent polymer or the copolymer containing more than 50 weight % of aromatic vinyl unimer, can be used. As regards the aromatic vinyl unimer, styrene, α - methyl styrene, m - methyl styrene, p - methyl styrene, o - chloro styrene, m - chloro styrene, p - chloro styrene, m - bromo styrene, p - bromo styrene etc. can be given, however, styrene is particularly desired to be used.

Moreover, as regards the examples of unimer that is copolymerized with aromatic vinyl unimer, unsaturated nitrile ring such as acrylonitrile, methacrylonitrile; methacrylic acid alkyl esters such as methyl methacrylate, n - propyl methacrylate, iso - propyl methacrylate, n - butyl methacrylate, cyclo hexyl methacrylate; acrylic acid esters such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate etc. can be given and further, methacrylic acid, acrylic acid, anhydrous maleic acid, anhydrous citraconic acid, N - methyl maleimide, N

- phenyl maleimide etc. can be given.

These unimers that are copolymerized, can be used independently or as a mixture. However, these are mixed or used within the range such that the transparency of copolymer formed with aromatic vinyl unimer, as well as resin material formed from it and polyphenylene ether, is not lost.

The aromatic vinyl unimer is desired to be contained in a quantity of more than 50 weight % in the unimer mixture. If it is contained in a quantity of less than 50 weight %, then moisture absorbance of the obtained resin increases which is not desired.

Moreover, as regards the fusion flowability of the polymer containing aromatic vinyl unimer as its main constituent, its melt flow rate (MFR) at 230°C and load of 3.8 kg should be within the range from 0.5 ~ 200, desirably, it should be 2 ~ 100.

If it exceeds 200, then mechanical strength lowers

whereas if it is less than 0.5, then it becomes difficult to decrease birefringence (double refraction) which is not desired.

As regards the manufacturing method of the polymer containing aromatic vinyl unimer as its main constituent, lump state polymerization, suspension polymerization, emulsification polymerization, solution polymerization, using radical initiator, can be given, however, lump state polymerization or suspension polymerization are desired from the point of obtaining polymer having satisfactory productivity and less mixing of impurities.

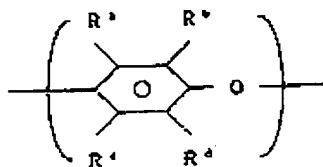
As regards the radical initiator, peroxides such as lauroyl peroxide, benzoyl peroxide, di - tert - butyl peroxide, di cumyl peroxide etc., azo compounds such as 2, 2' - azo bis iso butylonitrile, 1, 1' - azo bis (1 - cyclo hexane carbonitrile) etc. can be given.

Moreover, in order to regulate the molecular weight, tert - butyl, n - butyl, n - octyl, n - do decyl and tert

- do decyl mercaptan etc. can be added as chain transfer agent, as per requirement.

Polymerization is generally carried out at the temperature of 50 ~ 150°C.

Polyphenylene ether used in the present invention is the polymer possessing repetitive units shown by general formula given below.



(Here, R^a, R^b, R^c and R^d show hydrogen, halogen or hydrocarbon radical.)

The polyphenylene ether mentioned above is the polymer obtained by polymerizing phenol group unimer by oxidative coupling, and it is manufactured by well-known methods using copper group or manganese group catalyst, that are described in Patent number Sho 36 - 18692, Sho 47 - 36518, Sho 48 - 17396, Sho 49 - 16120, Sho 57 - 44623, Sho 57 - 147517, Sho 58 - 19329, Sho 58 - 19329, Sho 58 - 19330, Sho 63 - 91232

Sho 58 - 122919.

As regards the concrete examples of this polyphenylene ether, poly (2, 6 - di methyl - 1, 4 - phenylene) ether, poly (2 - methyl - 6 - ethyl - 1, 4 - phenylene) ether, poly (2 - methyl - 6 - propyl - 1, 4 - phenylene) ether, poly (2,6 - di propyl - 1, 4 - phenylene) ether, poly (2 - methyl - 6 - bromo - 1, 4 - phenylene) ether etc. can be given, however, poly (2, 6 - di methyl - 1, 4 - phenylene) ether is particularly desired to be used.

Moreover, as regards this polyphenylene ether, material generally used as engineering plastic can be used, however, material having low molecular weight is appropriate.

The block copolymer or graft copolymer formed from polymer component containing aromatic vinyl unimer as its main constituent and polyphenylene ether component, is obtained by polymerizing one unimer under the presence of the other.

Concretely, graft copolymer or block copolymer can be

manufactured by the method described in Patent number Sho
42 - 22069, Sho 47 - 1210, Sho 47 - 47862, Sho 52 - 38596
etc., in which unimer containing aromatic vinyl unimer as
its main constituent is polymerized under the presence of
polyphenylene ether, or phenol group unimer is subjected
to oxidative coupling polymerization under the presence
of polymer containing aromatic vinyl unimer units as its
main constituent.

As regards the proportion of polymer containing
aromatic vinyl unimer units as its main constituent and
polyphenylene ether, proportion of the former should be
within the range from 30 ~ 70 weight %, desirably, within
the range from 40 ~ 55 weight % and the proportion of latter
should be within the range from 30 ~ 70 weight %, desirably,
within the range from 45 ~ 60 weight %.

If polyphenylene ether component is less than 40
weight % or more than 70 weight %, then birefringence
(double refraction) of the optical element does not lower

sufficiently.

Moreover, if it less than 40 weight %, then sufficient heat resistance is not obtained.

In the resin composite, molding method is appropriately chosen within the range mentioned above.

The stabilized polyphenylene ether used in the present invention, is the material obtained by performing refining treatment to remove impurities, particularly quinone contained in polyphenylene ether, or the material obtained by performing the treatment of capping the terminal hydroxide radicals of polyphenylene ether and substituting it by inert stable radical, as well as material obtained by performing both these treatments.

As regards the method to perform refining treatment on polyphenylene ether, the method of using organic solvent having saturation of impurities more than that of polyphenylene ether, can be used.

As regards this organic solvent, α pinene is used.

The method in which polyphenylene ether prepared by the treatment with α pinene mentioned above is temporarily dissolved and is deposited using the difference in the solubility depending on temperature difference is used.

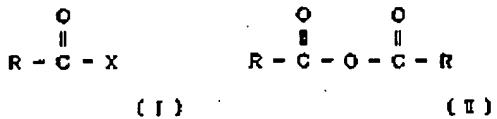
Dissolution temperature is within the range from 50 $^{\circ}$ C ~ 160 $^{\circ}$ C and deposition temperature is within the range from normal temperature ~ 0 $^{\circ}$ C.

Moreover, deposition by poor solvent can be carried out.

In the case of block copolymer or graft copolymer of polyphenylene ether, similar treatment can be carried out in the state of insoluble component remained present as a residue.

As regards the method to cap terminal hydroxide radicals of polyphenylene ether and substitute these with an inert radical, the method in which polyphenylene ether is treated with acylation agent, is used.

As regards the acylation agent, compound shown by the general formula given below can be used.



(Wherein, R is alkyl, aryl, cyclo alkyl or their mixture and X is chlorine, bromine, fluorine or iodine.)

As regards the acylation agent, mono acyl halide of [I] such as acetyl fluoride, acetyl chloride, acetyl bromide, propionyl halide, butylyl halide, stearoyl halide, benzoyl chloride, toluoyl halide, naphthoyl halide, sinamoyl (?) halide, or mono carbonic acid anhydride of [II] such as acetic acid anhydride, propionic acid anhydride, octanoic (caprylic) acid anhydride, benzoic acid anhydride, toluyl acid anhydride, butyric acid anhydride, bi valine acid anhydride, m - di chloro benzoic acid anhydride, 2, 3, 4, 5, 6 - penta chloro benzoic acid anhydride, pentanoic acid anhydride, palmitic acid anhydride, stearic acid anhydride etc. can be given.

This acylation agent is brought into contact with polyphenylene ether under the presence of basic aqueous

solution or catalytic phase transfer agent.

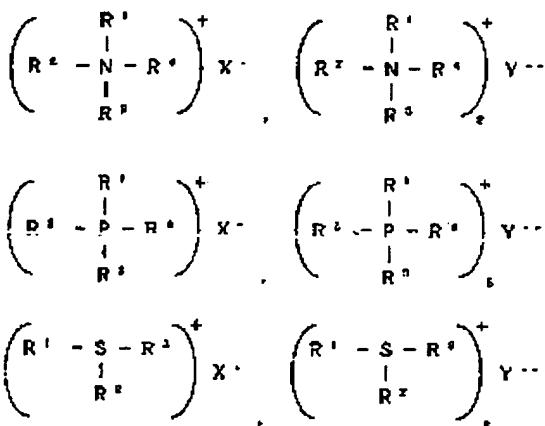
Quantity of acylation agent is theoretical quantity of hydroxide radicals of polyphenylene ether or slightly excess quantity.

As regards the basic material of basic aqueous solution, hydroxides, carbonate salts of alkali metals, or hydroxides of alkaline earth metals can be used and concretely, potassium hydroxide, sodium hydroxide, sodium carbonate, barium hydroxide etc. can be given.

This basic substance is used in a quantity, in terms of molar ratio, of acylation agent / basic substance = 1 / 100 ~ 50 / 1.

Moreover, as regards the catalytic phase transfer agent, quaternary ammonium salt, quaternary phosphonium salt and tertiary sulfonium salt or their mixture can be used.

Concretely, compounds shown by the formulae given below can be used.



(Wherein, R^1 , R^2 , R^3 and R^4 are aliphatic hydrocarbon radical, X^- is mono basic acid radical such as $C_6H_5^-$, Br^- , F^- , $CH_3SO_3^-$, $CH_3CO_2^-$, $CF_3CO_2^-$, or OR^- and Y^{--} shows dibasic acid radical such as SO_4^{2-} , CO_3^{2-} , $C_2O_4^{2-}$, etc.)

The quantity with which this catalytic phase transfer agent is used is within the range from $1 / 10 \sim 1 / 1000$, with respect to the quantity of basic substance, in terms of molar ratio.

Moreover, acylation reaction is carried out at the temperature within the range from $0 \sim 150^\circ C$ or more than that, however, it is desired to be carried out at the temperature within the range from $50 \sim 100^\circ C$.

As regards the other method to cap the terminals of polyphenylene ether using acylation agent such as mono carbonic acid anhydride such as acetic acid anhydride, the method in which polyphenylene ether is completely dissolved in organic solvent such as xylene, benzene, chloroform etc. with the concentration of more than 1 weight % and at least 1 type of metal chosen from zinc, tin, aluminium, cadmium and magnesium, as reducing agent and mono carbonic acid such as acetic acid are added to the solution mentioned above and then, reduction is progressed by shaking or stirring this solution at room temperature or the temperature more than that and capping is carried out by adding mono carbonic acid such as acetic acid anhydride with the quantity or twice the quantity equivalent to terminal hydroxide radicals of polyphenylene ether present in this solution, and polyphenylene ether is stabilized, is used.

Moreover, in the case of block copolymer or graft

copolymer possessing polyphenylene ether component also, same treatment is performed and polyphenylene ether component is capped.

Average molecular weight of the stabilized polyphenylene ether is expressed by limiting viscosity of the polymer (measured at 25°C in chloroform) and it is desired to be within the range from 0.1 ~ 1.0 and more desirably, it should be within the range from 0.3 ~ 0.7. Further desirably, it should be within the range from 0.3 ~ 0.45 and particularly desirably, it should be within the range from 0.35 ~ 0.42.

If it is less than 0.3, then mechanical strength of the optical element lowers.

In order to mix the polyphenylene ether thus stabilized and polymer containing aromatic vinyl unimer units as its main constituent, fusion mixing or solution mixing is appropriate to be used.

Fusion mixing is carried out at the temperature above

the glass transition temperature of polyphenylene ether under high shear using mixing devices such as extruder, bombarding mixer, kneader blender, heating roll etc.

As regards the extent of mixing, both the polymers are desired to be dispersed up to less than approximately 1 μ mutually and further, these are desired to be mixed up to the molecular scale.

Whether the mixing conditions are reached up to the molecular scale or not is easily determined when the mixture becomes the material having only one glass transition temperature.

In order to obtain sufficient and satisfactory mixing conditions, the method in which mixing temperature is increased and mixing period is stretched and further, shear strength is increased, is used.

Furthermore, in the fusion mixing, organic solvent can be used in small quantity as plasticizer in order to lower the glass transition temperature of both the polymers and

make the mixing easy.

As regards the organic solvent, organic solvents used in the solution mixing mentioned below can be used and after the completion of mixing, the used organic solvent can be removed by evaporation.

In the solution mixing, either solution of at least 1 weight % is formed by dissolving both the polymers in an organic solvent and homogeneous mixture is formed by carrying out stirring mixing and after that, organic solvent is removed by evaporation, or poor solvent of both the polymers is put in the homogeneous mixture and both the mixed polymers are deposited.

As regards the appropriate organic solvent, chloroform, methylene chloride, ethylene chloride, toluene, benzene, chloro benzene etc. can be given. Moreover, as regards the poor solvent, methanol, ethanol, propyl alcohol, n - hexane, n - pentane etc. can be given.

Moreover, stabilizer can be added in order to further

increase the thermal stability of resin composite of the present invention.

As regards this stabilizer, among the stabilizers used in synthetic resins, steric hindrance phenol compound, organic phosphorous acid group, organic phosphoric acid group compounds are appropriate to be used.

As regards the representative examples of steric hindrance phenol compound, 2, 6 - di - tert - butyl - p - cresol, 2, 2' - methylene - bis (4 - methyl - 6 - tert - butyl phenol), 1, 3, 5 - tris (4 - tert - butyl - 3 - hydroxy - 2, 6 - di methyl benzyl) iso cyanic acid, penta erythritol tetra quis [3 - (3, 5 - di - tert - butyl - 4 - hydroxy phenyl) propionate] etc. can be given.

As regards the organic phosphorous acid, organic phosphoric acid group compound, compound shown by the general formula given below can be used.



(Wherein, among R⁵, R⁶ and R⁷, at least 1 is - OR^R and others are organic radicals. Moreover, OR^R is hydrogen bond or organic radical and 2 or 3 among R⁵, R⁶ and R⁷ have bonded form.)

This stabilizer can be used jointly.

The quantity with which it is used is within the range from 0.01 ~ 3 parts by weight, with respect to 100 parts by weight of resin composite.

In order to mix this stabilizer with the resin composite, it can be mixed when carrying out fusion mixing or solution mixing to form the resin composite mentioned above.

Fusion molding in the present invention means molding carried out in the state of --- resin increasing more than the glass transition temperature.

For example, extrusion molding, compression molding etc. can be used.

Molding temperature is of the order of 350°C above the glass transition temperature of the resin.

(Effect / result of the invention)

In the resin formed from polymer containing aromatic vinyl unimer units as its main constituent and polyphenylene ether of the present invention, polyphenylene ether having deteriorating thermal stability has been stabilized and deteriorating by thermal history of high temperature at the time of carrying out molding, has been controlled and birefringence (double refraction) has been lowered due to which optical element having satisfactory light permeability can be obtained.

Moreover, process of increasing the properties of resin composite can be carried out, based on improving the thermal stability and increasing the process temperature and therefore, internal strain of the molded product, orientation of resin component can be lowered and optical element having more uniform light permeability and still lower birefringence (double refraction) can be obtained.

(Practical examples)

The present invention has been explained below in further details with the help of practical examples. However, the present invention is not restricted only to these practical examples.

Moreover, in the practical examples, "parts" or "%" are weight standards.

Moreover, properties indicated in practical examples were measured by following methods.

• Limiting viscosity of polymer: It was calculated by using Ubelhode viscometer over chloroform solution at 25°C.

• The endowment of fusion mixing and that of the hot ---- of the polymer was carried out by ---- at 280°C for durations of 5, 10 and 20 minutes (?).

• Light permeability: Press sheet of 1.2 mm was prepared from the powdered product of the composite at 290°C and permeability of test material having thickness of 1.2 mm

was measured at 800nm by spectrophotometer of Hitachi make 330 model.

• Molding of optical disk baseboard from the powdered mixture was carried out using Sumitomo Jukikai Kogyo Kabushiki Kaisha (Sumitomo Heavy Machinery Industries Ltd.) make Mat (?) 5/7 model as the injection molding machine and metallic mold used for disk of having thickness of 0.5 mm and molded material diameter of 50 mm, as the metallic mold.

• Foreign substances measurement: Black spots of the disk molded product having diameter of 30 mm and thickness of 0.5 mm obtained by injection molding was visually observed.

• Birefringence (double refraction): It was measured at the position of 15 mm from the center of the disk baseboard mentioned above by the Celmon (?) Compensator at 545 nm using diffused light microscope.

Practical examples 1 ~ 3

As per the method described in practical example 2, No. 9 of Patent number Sho 47 - 36518, poly (2, 6 - di methyl - 1, 4 - phenylene) ether having limiting viscosity of 0.45 was prepared by polymerizing 2, 6 - xlenol using manganese chloride and ethanol amine as solvents.

200 g of this polyphenylene ether was completely dissolved in 1 l of toluene and then, 200 ml of 10 % toluene solution of tetra butyl ammonium chloride and 100 g of 50 % aqueous solution of sodium hydroxide were added to it.

This mixture was vigorously stirred for 5 minutes under nitrogen atmosphere and the solution formed from 100 ml of acetic acid anhydride and 150 ml of toluene was added to it extending over 10 minutes.

After this, this solution was added to methanol and polymer was deposited and recovered.

This polymer was washed with methanol and then dried and acetic acid capped polymer was obtained.

Limiting viscosity of this polymer was 0.40.

The resin composite formed from 52 parts of this capped polyphenylene ether and 48 parts of Esprite (?) 1-62 A (Sumitomo Kagaku Kogyo (Sumitomo Chemical Industries) make) as polystyrene was sufficient mixed and fusion mixed and evaluated.

The results have been presented in table 1 given below.

Practical examples 4 ~ 6

200 g of poly (2, 6 - di methyl - 1, 4 - phenylene) ether same as that of practical example 1 was completely dissolved in 1 l of toluene and 10 go of zinc powder and 200 ml of 50 % aqueous solution of acetic acid were mixed with this solution and it was vigorously stirred and then, the solution formed from 100 ml of acetic acid anhydride and 150 ml of toluene was added and reaction was carried out.

After the completion of reaction, zinc powder present in the solution was removed by membrane filter and this reaction solution was added to 3 l of methanol and polymer

and deposited and recovered.

This polymer was washed with methanol and then dried and acetic acid capped polymer was obtained.

Limiting viscosity of this polymer was 0.40.

It was treated by the procedure same as that of practical examples 1 ~ 3.

Practical example 7 ~ 3

Poly (2, 6 - di methyl - 1, 4 - phenylene) ether having limiting viscosity of 0.40 was prepared similar to practical example 1.

200 g of this polymer was completely dissolved in 500 ml of α - pinene at 160°C .

This solution was cooled up to room temperature and polymer was deposited and it was filtered by membrane filter and refined polymer was obtained.

This polymer was washed with methanol and then dried and acetic acid capped polymer was obtained.

Limiting viscosity of this polymer was 0.40.

It was treated by the procedure same as that of practical examples 1 ~ 3.

The results have been presented in table 1 given below.

Comparative examples 1 ~ 3

Poly (2, 6 - di methyl - 1, 4 - phenylene) ether same as that used in practical example 7 was mixed with polystyrene without performing any treatment. Other than this change, procedure same as that of practical examples 1 ~ 3 was carried out.

The results have been presented in table 1 given below.

Table 1

	Mixing time (minutes)	Foreign substance (units)	Birefringence (double refraction) (nm)	Light permeability (%)
Practical example 1	5	0	+1	93
2	10	1	+1	92
3	20	1	+2	92

4	5	0	+1	94
5	10	0	+1	94
6	20	1	+2	92
7	5	5	+6	83
8	10	11	+10	83
9	20	15	+13	70
Comparative example 1	5	12	+7	81
2	10	20	+15	72
3	20	47	+51	60